

Contribution # 62

Determination of Polychlorinated Dibenzo-P-Dioxins
and Polychlorinated Dibenzofurans
in FVP Sediment Samples

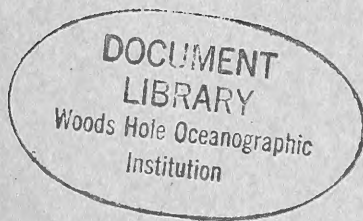
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Disposal Area Monitoring System DAMOS

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US Army Corps
of Engineers
New England Division



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DIBENZO-P-DIOXINS AND
POLYCHLORINATED DIBENZOFURANS
IN FVP SEDIMENT SAMPLES**

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AUGUST 1988

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INTRODUCTION

In 1982 a large cooperative study was initiated between the U.S. Army Corps of Engineers' Waterways Experiment Station, Vicksburg, MS (WES) and the U.S. Environmental Protection Agency's Environmental Research Laboratory, Narragansett, RI (ERL-N). This study, called the Field Verification Program (FVP), was designed to investigate three options to the disposal of contaminated dredged material and the adequacy of biological laboratory testing procedures for predicting actual field measured responses.

The source of the dredged sediment used for the study was Black Rock Harbor (BRH) in Bridgeport, CT. WES investigated the effects of disposal at both upland and wetland sites and ERL-N investigated effects associated with the aquatic disposal of this material at the Central Long Island Sound (CLIS) disposal site. Munns et al. (In preparation) describes the aquatic portion of the study in considerable detail.

Field studies were carried out at all three sites, and laboratory experiments were conducted at both WES and ERL-N. For the laboratory studies it was necessary to collect a large and representative composite dredged material sample. This was accomplished by collecting sediment to dredging depth with a large box core at stations all along the channel to be dredged. Figure 1 shows a representation of the study area and the location of aquatic disposal at the Central Long Island Sound Disposal Site.

The sediment collected from the dredging area for the laboratory studies was placed into a commercial cement mixer for homogenization. This composite sediment was then placed in a series of 55 gallon drums; the drums of BRH material were transported to WES and ERLN and refrigerated.

The contaminant concentrations in this BRH sediment composite have been extensively characterized (Rogerson et al., 1985) at ERL-N. In addition, a sample of this material was transported to the U.S. Environmental Protection Agency's Environmental Research Laboratory at Duluth, MN (ERL-D) in September of 1986 for the analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Preliminary results from these analyses indicated very high levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-tetra-CDD). This caused concern because this compound is one of the most toxic compounds known for some species. Further analysis was therefore warranted to confirm these results or detect possible contamination or analytical problems. The final results from this initial sample and the results of subsequent analyses

that have been conducted on the BRH composite sample at ERL-D have shown that the concentration of 2,3,7,8-tetra-CDD is much lower than the preliminary results indicated. However, this material does contain numerous PCDD and PCDF compounds (ERL-D, unpublished data).

The purpose of the present study was to measure the levels of PCDDs and PCDFs in five archived sediment samples from Black Rock Harbor in Bridgeport, CT and Central Long Island Sound in order to confirm the results from ERL-D. The five samples analyzed included a sample of the original BRH composite sediment, dredged material collected from the wetland and upland disposal sites, and two sediment core samples from the CLIS disposal area. The samples chosen from CLIS included one from the 4-6 cm section of a sediment core taken from 200 meters east of the FVP disposal mound center on BRH dredged material. This sample was chosen because it contained the highest PCB concentration (Munns et al., In preparation) on the last sampling date (10/22/85) of the FVP study. It was selected to represent potentially a worst case condition now existing at the CLIS disposal site. In addition, a sample of the 4-6 cm section of a sediment core from the Reference station was also chosen for comparison. This sample should represent background levels in Central Long Island Sound.

Analysis of all five samples was performed by Battelle Columbus Laboratories (Columbus, Ohio); the concentrations of PCDDs and PCDFs measured in these samples are reported. The analytical procedures used to obtain the results are described, and a discussion of the results in comparison with those reported by other studies is included.

ANALYTICAL METHODOLOGY

Sample Extraction and Analyte Enrichment

Eleven gram aliquots of dried sediment samples were weighed by difference into Soxhlet extraction thimbles and spiked with the stable carbon isotopes of PCDDs and PCDFs listed in Table 1. The Soxhlet extractors were assembled and the samples extracted for 18 hours with 250 ml of benzene. After extraction, the benzene extracts were concentrated to approximately 5 ml with 3-stage Snyder columns. Laboratory method blank and native spike samples were prepared with the samples.

The sample extracts were diluted to 10 ml with hexane and washed with three 10 ml aliquots of concentrated sulfuric acid. The combined acid washes were extracted with hexane and

then combined with the sample extract, and concentrated to 5 ml. The extracts were then transferred to a tandem arrangement of silica gel columns containing activated silica gel, 44 percent concentrated sulfuric acid on silica gel, and 33 percent 1M sodium hydroxide on silica gel. The purpose of these columns was to remove acidic and basic compounds and easily oxidized materials from the extracts. The silica gel support provided a large surface area for contact with the sample extracts, thus improving the cleanup efficiency. The PCDD/PCDF isomers were eluted from the columns with 70 ml of hexane and the entire eluates, including the original extract volume, were collected. The hexane eluates were concentrated to 2-3 ml with a gentle stream of nitrogen gas.

Elemental sulfur, naturally occurring in sediments, was removed by shaking with an aqueous solution of tetrabutylammonium sulfite. The hexane solutions were dried with sodium sulfate and chromatographed through columns containing approximately 5 g of activated basic alumina with hexane/methylene chloride (97:3, v/v), and hexane/methylene chloride (1:1, v/v) as elution solvents. The eluates were collected, concentrated to near dryness and then diluted to 2 ml with hexane. Because the sediment extracts were still highly colored and contained precipitated material, the hexane solutions were chromatographed through columns containing 1 g of activated florisil. The columns were eluted with 15 ml of hexane, 25 ml of ethyl ether/hexane (6:94, v/v) and 75 ml of methylene chloride/hexane (3:1, v/v). The 3:1 methylene chloride/hexane eluates were collected, concentrated to near dryness, and dissolved in 50 μ l of n-decane containing 5 ng of an absolute recovery standard, 2,3,7,8-tetrachlorodibenzo-p-dioxin-³⁷Cl₄ (2,3,7,8-tetra-CDD-³⁷Cl₄). All solutions were stored at 0°C and protected from light until analyzed.

Analysis

The extracts were analyzed and quantified for PCDD/PCDF by combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The HRGC/HRMS system consists of a Carlo Erba Model 4160 gas chromatograph interfaced directly into the ion source of a VG Model 7070 high resolution mass spectrometer. The chromatographic column was a 60 M DB-5 fused silica column. Helium was used as the carrier gas at a flow velocity of 30 cm/sec. The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 9,000-12,000 (M/ Δ M, 10 percent valley definition). The operating parameters of the HRGC/HRMS system are summarized in Table 1. All HRGC/HRMS data were acquired by multiple-ion-detection (MID) with a VG Model 11-250J Data System. The exact masses that were monitored are shown in Table 3.

Quality Assurance

The operation of the HRGC/HRMS was evaluated each day by analyzing standard mixtures of PCDD/PCDF isomers. These mixtures consisted of 2,3,7,8-tetra-CDD, 2,3,7,8-tetra-CDF, 2,3,7,8-tetra-CDD-¹³C₁₂, and 2,3,7,8-tetra-CDF-¹³C₁₂ to evaluate accuracy of quantification and to evaluate isomer resolution. Mixtures of selected PCDD/PCDF isomers were used to evaluate the stability of the chromatographic elution windows. The mass focus accuracy of the MID unit was evaluated before each analysis by observing selected ion masses from perfluorokerosene (PFK). Adjustments were made to the offset to correct for minor variations. Mass focus stability was assured by use of a reference PFK "lock mass" to correct for any mass focus drift.

Native spike and a laboratory method blank samples were processed during the extraction and cleanup of the samples. For the native spike, isotopically labeled compounds were added to the Soxhlet thimble with no sediment added. The compounds and amounts added are listed in Table 4. The native spike samples were used to evaluate the accuracy of quantification, while the laboratory method blanks were used to demonstrate freedom from contamination. The results of these analyses are summarized in Table 4. The analyses of the method blanks were free of PCDD/PCDF contamination except for traces of hepta- and octa-CDD/CDF.

Recovery of the spiked PCDD/PCDF standards from the native spike samples ranged from 62-110 percent, which is within the expected range of variation for a sample subjected to florisil chromatography. Replicate analyses were not done as part of this study, but the precision of these analyses are generally about ± 20-30%.

Recovery of Internal Standards

Recoveries of the internal standards, 2,3,7,8-tetra-CDD-¹³C₁₂, 1,2,3,7,8-penta-CDD-¹³C₁₂, 1,2,3,6,7,8-hexa-CDD-¹³C₁₂, 1,2,3,4,6,7,8-hepta-CDD-¹³C₁₂, 1,2,3,4,6,7,8,9-octa-CDD-¹³C₁₂, 2,3,7,8-tetra-CDF-¹³C₁₂, 1,2,3,7,8-penta-CDF-¹³C₁₂, 1,2,3,4,7,8-hexa-CDF-¹³C₁₂ and 1,2,3,4,6,7,8-hepta-CDF-¹³C₁₂ were calculated by comparison to the external standard, 1,2,3,4-tetra-CDD-¹³C₁₂, which was added following extraction. Relative response factors were determined from four analyses of a standard mixture containing the eight isotopically labelled standards. The equation used to calculate the recoveries was:

$$\text{Recovery (\%)} = \frac{\text{Ais} \times \text{Qrs} \times 100}{\text{Ars} \times \text{Qis} \times \text{Rf}}$$

Where:

Ais = Sum of integrated areas for internal standard;
Qrs = Quantity of recovery standard in ng;
Ars = Sum of integrated areas for recovery standard;
Qis = Quantity of internal standard in ng; and
Rf = Response factor.

Quantification

The PCDD/PCDF isomers were quantified by comparing the sum of the two ions monitored for each class to the sum of the two ions monitored for a corresponding isotopically labelled congener. The octa-CDD- $^{13}\text{C}_{12}$ was used to quantify the octa-CDF. Experimental relative response factors were calculated from four analyses of a mixture which contained representatives of the tetrachloro- through octachloro- PCDD/PCDF congener classes. These response factors were included in all calculations used to quantify the data. The response factors were calculated by comparing the sum of the two ions monitored for each congener class to the sum of the two ions monitored for the corresponding internal standard. The experimental response factors were:

<u>Congener Class</u>	<u>Response Factor</u>
Tetra-CDD	0.91
Penta-CDD	1.0
Hexa-CDD	0.84
Hepta-CDD	0.91
Octa-CDD	0.89
Tetra-CDF	0.92
Penta-CDF	0.92
Hexa-CDF	0.85
Hepta-CDF	0.93
Octa-CDF	0.89

The formula used for quantifying the PCDD/PCDF isomers was:

$$\text{Concentration (ng/g)} = \frac{\text{Ac} \times \text{Qis}}{\text{Ais} \times \text{W} \times \text{Rf}}$$

where:

Conc. = Concentration in parts-per-billion (ng/g) of target isomer or congener class.

Ac = Sum of integrated areas for the target isomer or congener class;

Qis = Quantity of internal standard in ng;

Ais = Total integrated areas for the internal standard;

W = Sample weight in g; and

Rf = Response factor.

Each pair of resolved peaks in the selected-ion-current chromatograms was evaluated manually to determine if it met the criteria for a PCDD or PCDF isomer. By examining each pair of peaks separately, quantitative accuracy was improved over what is obtained when all of the peaks in a selected chromatographic window are averaged. When averaged data are used, it is possible for pairs of peaks with high and low chlorine isotope ratios to produce averaged data that meets the isotope ratio criterion. For example, two pairs of peaks having chlorine isotope ratios of 0.56 and 0.96, both outside of the acceptable range, would have an average ratio of 0.76.

The criteria that were used to identify PCDD and PCDF isomers were:

- (1) Simultaneous responses at both ion masses;
- (2) Chlorine isotope ratio within $\pm 15\%$ of the theoretical value;
- (3) Chromatographic retention times within windows determined from analyses of standard mixtures;
- (4) Signal-to-noise ratio equal to or greater than 2.5 to 1.

The 2,3,7,8-substituted PCDD/PCDF isomers and the octa-CDD included the additional criterion that they coeluted within ± 2 seconds of their isotopically labelled analogs.

A limit of detection (LOD) was calculated for samples in which isomers of a particular chlorine congener class were not detected. The formula used for calculating the LOD was:

$$\text{LOD (ng/g)} = \frac{\text{Hc} \times \text{Qis} \times 2.5}{\text{His} \times \text{W} \times \text{Rf}}$$

where:

LOD = Single isomer limits of detection (ng/g) for a congener class;
Hc = Height of congener class isomer;
Qis = Quantity of internal standard (ng);
His = Peak height of internal standard;
W = Sample weight (g)
Rf = Response factor; and
2.5 = Signal-to-noise ratio.

RESULTS

Isomers of PCDD/PCDF's were detected at all sample locations, higher levels of PCDD/PCDF were found in the composite, wetland and upland samples, compared with the 200 East (2E8510) and South Reference (RS8510) samples (Table 4). This table also includes information on the recovery of congeners spiked into a sample and the method blank levels. The procedural blank levels were either not detectable or insignificant measurable levels of some PCDDs and PCDFs were found in all of the samples analyzed (Table 4) and, therefore, the sample results have not been corrected for laboratory or field blank levels. They have been corrected, however, for extraction efficiency and cleanup losses. A detection limit is listed for samples in which a particular congener was not detected. The concentration of the 2,3,7,8-substituted PCDD/PCDF which coeluted with the internal standards are also given in Table 4. In some cases, as indicated in Table 4, the peaks quantified could include more than one compound. On the DB-5 capillary gas chromatographic column 2,3,7,8-tetra-CDF, 1,2,3,7,8-penta-CDF, 1,2,3,6,7,8-hexa-CDF, and 1,2,3,4,7,8-hexa-CDF are not easily resolved from certain other isomers in their congener class, and thus, may contain contributions from other isomers. For example, 2,3,7,8-tetra-CDF may coelute with 1,2,4,9-tetra-CDF, 2,3,4,7-tetra-CDF, 2,3,4,8-tetra-CDF, and 2,3,4,6-tetra-CDF.

The number of resolved peaks quantified as PCDD/PCDF in each congener group are given in Table 5. Each resolved peak may contain more than one CDD/CDF isomer. The octa- CDD/CDF, for which there exists only one isomer of each class, are not listed in Table 5. Several isomers were observed for most congener classes. In general, hepta-and octa-CDD/CDF were the most abundant congener classes in the sediment samples (Table 4).

The recovery of tetra- through octa- CDD/CDF averaged 61 percent (Table 6), which is within the expected range of recoveries for samples subjected to florisil chromatographic cleanup. Chlorine isotope ratios for samples that contained PCDD/PCDF isomers are summarized in Table 7, and all met acceptance criteria.

DISCUSSION

Few studies have measured the concentrations of PCDDs and PCDFs in sediments, especially marine sediments. This is mainly because of the level of difficulty associated with the chemical analyses and the lack of appropriate instrumentation. The instrumentation utilized (preferably high resolution gas chromatography-mass spectrometry) must be sensitive enough to measure picogram quantities of compounds in the sample extracts and be able to definitively identify the compounds to the specific congener. This is particularly difficult, because chlorinated compounds from several chemical classes (biphenyls, biphenylenes, naphthalenes and diphenyl ethers) are found in environmental samples and show very similar fragmentation patterns. Many of these compounds such as polychlorinated biphenyls (PCBs) are found in concentrations considerably higher than those of the PCDDs and PCDFs. For example, the concentration of PCBs as Aroclor 1254 in the BRH Original Composite is about 7000 ng/g (Munns et al., In preparation). This is about 350 times the total PCDD concentration and 1000 times the PCDF levels measured in that sediment in the present study (Table 4).

There are 75 possible congeners of PCDDs and 135 potential PCDF compounds. Generally, not all of these compounds are found in environmental samples with the possible exception of fly ash (Karasek and Hutzinger, 1986). However, sediments can contain numerous PCDDs and PCDFs in measurable quantities. Table 4 shows that as many as 16 different PCDD and 41 PCDF peaks were found in measurable quantities in some of the samples. This means that many different compounds were present. More compounds than this were possibly present because some of the compounds coelute as a single peak (Table 4).

Measurable concentrations of PCDDs and PCDFs were detected in all four of the BRH sediment samples and the Reference station sample (Table 4). The sum or total concentrations of all of the measured PCDDs were highest and similar in the BRH Original Composite, BRH Wetland, and BRH Upland samples. The 200 East sample contained lower levels and the lowest total PCDD concentration was found at the South Reference site.

The same trend was also observed for the total PCDF concentrations. The levels were highest and similar in the BRH Original Composite, BRH Wetland and BRH Upland samples. The 200 East sample had a lower total PCDF concentration and the lowest level was measured in the South Reference sample; however, there

was little difference between the total PCDF concentrations of the 200 East and South Reference samples.

The 2,3,7,8-substituted congeners are considered to be the most environmentally significant compounds (Kuehl et al., 1987) for both the PCDDs and PCDFs. This is because these compounds are preferentially accumulated by organisms and are the most toxic. The concentration of one 2,3,7,8 substituted compound was measured for each level of chlorination for both series of compounds.

The compound, 2,3,7,8-tetra-CDD, is generally considered to be the most toxic of all of the compounds measured in this study (Safe et al., 1986). Only the BRH Wetland sample contained a measurable concentration of this compound. The measured 2,3,7,8-tetra-CDD concentration in this sample was 0.043 ng/g (compared to the suggested criteria of 1 ng/g). However, since the detection limits for the BRH Original Composite and BRH Upland samples were higher than this level (0.078 and 0.11 ng/g, respectively), these samples may have contained similar concentrations of 2,3,7,8-tetra-CDD.

The detection limit achieved for a sample is dependent on the level of interferences or the 'matrix' of the sample. That is why the detection limits vary from sample to sample. For less complex samples with lower levels of contamination, such as the South Reference sample, lower detection limits are generally achieved as was seen in this study.

The ERL-D laboratory measured the concentrations of numerous congeners in the BRH Original Composite including the 2,3,7,8-substituted congeners measured here (Table 8). In general, there is excellent agreement between the data from the present study and the ERL-D results. The possible exception to this is for 2,3,7,8-tetra-CDF. The result reported in this study is considerably higher than the ERL-D data. This difference is probably due to incomplete resolution of the various tetra-CDFs in the present study.

Only two other studies could be found that report the concentrations of PCDDs or PCDFs in estuarine or marine sediments. Belton et al. (1985) reported the levels of 2,3,7,8-tetra-CDD in the sediments of the Passaic River, New Jersey. This area was sampled because very high concentrations of 2,3,7,8-tetra-CDD have been found in the soil around a chemical plant that manufactured Agent Orange. It has been shown that 2,3,7,8-tetra-CDD is a major contaminant in Agent Orange. The sediments of the Passaic River around this facility contained 2,3,7,8-tetra-CDD concentrations as high as 6.9 ng/g. Sediments from other areas of the river had levels ranging from 0.13 to 1.2 ng/g.

O'Keefe et al. (1984) reported the concentrations of 2,3,7,8-tetra-CDD and 2,3,7,8-tetra-CDF in sediments at three locations in the Hudson River. The levels that they reported ranged from <0.0056 to 0.010 ng/g for 2,3,7,8-tetra-CDD and from 0.005 to 0.046 ng/g for 2,3,7,8-tetra-CDF. The highest levels were found in the lower portion of the river. The 2,3,7,8-tetra-CDD concentration measured in the BRH Wetland sample is higher than the levels measured in the Hudson River. Because of the problems with coelution of the tetra-CDFs in the present study, it is not possible to compare the results for 2,3,7,8-tetra-CDF.

Kuehl et al. (1987) reported the concentrations of 2,3,7,8-tetra-CDD in freshwater sediments from the Wisconsin River and Petenwell Reservoir (not used for potable water) in Wisconsin. The Wisconsin River sediment had a 2,3,7,8-tetra-CDD concentration of 0.039 ng/g and the Petenwell Reservoir sediment had a level of 0.17 ng/g. The former is similar to the concentration reported in the BRH Wetland sample and the later is considerably higher. Kuehl et al. (1987) also quantified numerous other congeners of PCDDs and PCDFs including several of the 2,3,7,8-substituted congeners measured in the present study. The levels that they reported for the Petenwell Reservoir sediment were very similar to the results from the present study for both series of compounds.

Many of these same compounds were also quantified in the sediments of several rivers from an industrialized area in southwestern Germany and in Lake Constance (Hagenmaier et al., 1986). The 2,3,7,8-tetra-CDD and 2,3,7,8-tetra-CDF compounds were not detected in any of the river samples, although 2,3,7,8-tetra-CDF was detected at a level of 0.010-0.040 in Lake Constance sediments. This level, as well as the levels of all of the other congeners of both PCDDs and PCDFs measured in both studies, were similar to those found in the 200 East and South Reference sediments and lower than those of the BRH samples.

Several studies have measured the concentrations of PCDD and PCDF compounds as the sum of all compounds at each level of chlorination. Petty et al. (1983) measured the concentrations of PCDDs in the sediments of the Housatonic River in Massachusetts. The concentrations that they reported were generally similar to those measured at 200 East and South Reference in the present study and lower than the BRH samples. The total PCDF concentration that they measured was 1.35 ng/g.

Czuczwa and coworkers have published several papers on the levels of PCDFs and PCDDs in the Great Lakes. Hexa-, hepta- and octa-CDDs were found in the highest concentrations. The concentrations of total hexa-CDDs ranged from about 0.050 to 0.300 ng/g in Lake Huron, away from known areas of contamination, and was about 4.0 ng/g in the relatively contaminated area of Saginaw Bay (Czuczwa and Hites, 1984). The concentration of

hepta-CDDs were about 0.050 to 0.400 ng/g in Lake Huron and about 10.0 in Saginaw Bay. The concentrations of octa-CDD was measured in four of the Great Lakes (Czuczwa and Hites, 1984; Czuczwa and Hites, 1986). The levels ranged from about 0.30 to 4.8 ng/g except Saginaw Bay which had a concentration of about 35 ng/g. The levels measured in the present study were generally higher than those mentioned above except for the Saginaw Bay samples.

PCDFs at each level of chlorination could be detected in Lake Huron (Czuczwa and Hites, 1984). The concentrations of tetra-CDFs were generally lowest, ranging from about 0.080 to 0.200 ng/g away from Saginaw Bay and about 3.0 in Saginaw Bay. The hepta-CDFs were found in the highest concentrations. The range of concentrations found outside of Saginaw Bay was about 0.20 to 1.0 and in Saginaw Bay the concentration reached about 30 ng/g. Again, as with the PCDDs, the levels from the present study are similar, except the Saginaw Bay levels are much higher.

In addition, Czuczwa et al. (1984) measured the levels of PCDDs and PCDFs in the sediments of Siskiwit Lake which is on Isle Royale in Lake Superior. This site was chosen because atmospheric input is the only potential source of contaminant input. The concentrations of PCDDs and PCDFs at each level of chlorination were detectable but low. For the PCDDs, the hexa-CDD concentration in the surface sediment was lowest (0.010 ng/g) and the octa-CDD level was the highest (0.56 ng/g). The hepta-CDF concentration was lowest for the PCDFs and the hepta-CDF level was highest (0.020 ng/g). The levels found in the present study were generally lower than those measured in Siskiwit Lake for PCDDs and higher for PCDFs.

There has been considerable debate in the literature on the sources of these compounds to the environment. Hutzinger et al. (1985) presented an overview of PCDD and PCDF sources. Potential sources for these compounds include various chemical manufacturing processes and incomplete combustion. Bumb et al. (1980) published a very controversial paper which indicated that PCDDs are produced in virtually all combustion processes including natural forest fires. Many studies have shown that PCDDs and PCDFs are produced in municipal incinerators (Buser et al., 1978; Czuczwa and Hites, 1984 and references within) and Eitzer and Hites (1986) measured the concentrations of these compounds in atmospheric particulate and vapor phases. Some very recent work (Ballschmitter et al., 1986; Marklund et al., 1987) indicates that automobiles burning leaded gasoline may be the major source of PCDDs and PCDFs to the environment.

The ratios of congeners found in a sample can provide information on the source of the contamination. Hagenmaier et al. (1986) used this approach and concluded that the PCDDs found in several rivers in southwest Germany were associated with the use of pentachlorophenol.

Several congeners were found at each level of chlorination for both PCDDs and PCDFs in the samples from the present study. This information and the ratios of congeners indicate that the sources of these compounds are probably combustion processes. For example, particulates released in automobile exhaust and deposited on roads may be washed from road surfaces during rains and thereby enter Black Rock Harbor. This, however, is only speculation and many other sources of these compounds, such as power plants, incinerators and various industries, are also possible.

Assessing the effects of environmental levels of PCDDs and PCDFs is a very difficult task. Many of the compounds have been shown to produce toxic, teratogenic and carcinogenic effects in various organisms (Safe et al., 1986). Some congeners also show very high bioconcentration factors (Geyer et al., 1987). The effects of these compounds vary tremendously between congeners and between species tested. For example, the "no effect" level for fetotoxicity and teratogenicity to rats is 100 million times lower for 2,3,7,8-tetra-CDD than for 1,3,6,8-tetra-CDD (Karasek and Hutzinger, 1986). Similarly, the LD-50 for 2,3,7,8-tetra-CDD is 3500 ug/kg for the hamster and 0.6 ug/kg for the guinea pig (Karasek and Hutzinger, 1986). Little is known about the effects of these compounds on man (Tschirley, 1986). To complicate matters, there is large variability in the bioavailability of these compounds from different soils (Umbreit et al., 1986) and the accumulation of these compounds from sediments is dramatically different between congeners (Kuehl et al., 1987). In addition, very little is known about the effects of complex mixtures of these compounds.

In general, however, the 2,3,7,8-substituted congeners are bioconcentrated to the greatest extent (Kuehl et al., 1987) and are the most toxic. Safe et al. (1986) collected data on body weight loss, thymic atrophy and aryl hydrocarbon hydroxylase activity in rats. Their data would suggest the following ordered list of decreasing toxicity for several of the congeners quantified in the present study; 2,3,7,8-tetra-CDD > 1,2,3,7,8-penta-CDD > 1,2,3,4,7,8-hexa-CDF > 1,2,3,7,8-penta-CDF > 2,3,7,8-tetra-CDF.

Few guidelines exist for assessing the significance of various levels of PCDDs and PCDFs in sediments. The Center for Disease Control, however, did state that exposure to soil containing concentrations of 2,3,7,8-tetra-CDD above 1 ng/g could constitute a potential health risk (Belton et al., 1985). Also, the U.S. Food and Drug Administration (FDA) has set "Levels of Concern" for 2,3,7,8-tetra-CDD in fish. FDA recommends that fish with concentrations greater than 0.050 ng/g wet weight not be eaten. Only two meals per month should be consumed for fish

containing 2,3,7,8-tetra-CDD concentrations between 0.050 and 0.025 ng/g wet weight.

No studies have been conducted on the bioaccumulation from sediments of 2,3,7,8-tetra-CDD in marine organisms. However, Kuehl et al. (1987) found that the freshwater fish (Cyprinus caprio) collected from an area that had a sediment 2,3,7,8-tetra-CDD concentration of 0.17 ng/g contained 0.12 ng/g dry weight of this compound. Using only this data, extrapolating to BRH Wetland sediment levels and converting dry weight to wet weight concentrations (assuming a wet/dry ratio of 4) would predict a level of about 0.008 ng/g wet weight for fish constantly exposed to BRH Wetland sediment. This is below the FDA "Levels of Concern" of 0.025 ng/g. Obviously, however, this is only a highly speculative paper exercise which should only be used as a very rough estimate.

CONCLUSIONS

The toxic compound, 2,3,7,8-tetra-CDD, was detected in the BRH Wetland sample at a level of 0.043 ng/g, and was below the detection limits for the other four samples tested. The concentration of 2,3,7,8-tetra-CDD measured in the BRH Wetland sediment in this study is well below the level of 1 ng/g for soil listed by the Center for Disease Control as a level that constitutes a potential health risk.

Numerous PCDD and PCDF compounds were detected in all of the five samples analyzed in this study (BRH Original Composite, BRH Wetland, BRH Upland, 200 East and South Reference). The levels of PCDDs and PCDFs at the South Reference station are relatively low and probably represent general background levels resulting from the atmospheric and riverine deposition of these compounds. The levels measured in the BRH Original Composite, BRH Wetland and BRH Upland samples were considerably higher than those of the South Reference sediments. The sediment sample found to have the highest PCB concentrations at the FVP disposal site on the last FVP Study sampling date (10/22/85), the 4-6 cm sediment core section from 200 meters East of the disposal buoy, contained PCDD and PCDF concentrations only slightly above the levels measured in the South Reference sample.

The source of PCDDs and PCDFs to Black Rock Harbor is not known. However, the congener ratios indicate that combustion processes may be the major source of these compounds.

If 2,3,7,8-tetra-CDD in Black Rock Harbor sediment behaved similarly to what Kuehl et al. (1987) reported in a bioaccumulation study using freshwater fish and sediment, fish

exposed to BRH Wetland sediment would not accumulate 2,3,7,8-tetra-CDD concentrations above the FDA "Levels of Concern" for this compound. This is, however, a highly speculative estimate.

Black Rock Harbor sediment could probably be considered to be moderately contaminated with PCDDs and PCDFs compared to the few reported literature concentrations of these compounds in sediments. Because the BRH Original Composite is a homogenized sample, it is possible that higher concentrations of these compounds exist in some areas of Black Rock Harbor. The levels measured in the present study may be high enough to warrant studies of the spatial and vertical distributions of these compounds in the sediments of Black Rock Harbor.

REFERENCES

- Ballschmitter, K., H. Buchert, R. Niemczyk, A. Munder and M. Swerev. 1986. Automobile exhausts versus municipal-waste incineration as sources of the polychloro-dibenzodioxin (PCDD) and -furans (PCDF) found in the environment. *Chemosphere* 15: 901-915.
- Belton, T.J., R. Hazen, B.E. Ruppel, K. Lockwood, R. Mueller, E. Stevenson and J.J. Post. 1985. A Study of (2,3,7,8-tetrachlorodibenzo-p-dioxin) Contamination in Select Finfish, Crustaceans and Sediments of New Jersey Waterways. Office of Science and Research, New Jersey Department of Environmental Protection, CN-409, 101 pp.
- Bumb, R.R., W.B. Crummett, S.S. Cutie, J.R. Gledhill, R.H. Hummel, R.O. Kagel, L.L. Lamparski, E.V. Luoma, D.L. Miller, T.J. Nestrick, L.A. Shadoff, R.H. Stehl and J.S. Woods. 1980. Trace chemistries of fire: A source of chlorinated dioxins. *Science* 210: 385-390.
- Buser, H.R., H.-P. Bosshardt and C. Rappe. 1978. Identification of polychlorinated dibenzo-p-dioxin isomers in fly ash. *Chemosphere* 7: 165-172.
- Czuczwa, J.M. and R.A. Hites. 1984. Environmental fate of combustion-generated polychlorinated dioxins and furans. *Environmental Science and Technology* 18: 444-450.
- Czuczwa, J.M. and R.A. Hites. 1986. Airborne dioxins and dibenzofurans: Sources and fates. *Environmental Science and Toxicology* 20: 195-200.

- Czuczwa, J.M., B.D. McVeety and R.A. Hites. 1984. Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments from Siskiwit Lake, Isle Royale. *Science* 226: 568-569.
- Eitzer, B.D. and R.A. Hites. 1986. Concentrations of dioxins and dibenzofurans in the atmosphere. *International Journal of Environmental Analytical Chemistry* 27: 215-230.
- Geyer, H.J., I. Scheunert and F. Korte. 1987. Correlation between the bioconcentration potential of organic environmental chemicals in humans and their n-octanol/water partition coefficients. *Chemosphere* 16: 239-252.
- Hagenmaier, H., H. Brunner, R. Haag and A. Berchtold. 1986. PCDDs and PCDFs in sewage sludge, river and lake sediments from south west Germany. *Chemosphere* 15: 1421-1428.
- Hutzinger, O., M.J. Blumich, M.v.d. Berg and K. Olie. 1985. Sources and fate of PCDDs and PCDFs: An overview. *Chemosphere* 14: 581-600.
- Karasek, F.W. and O. Hutzinger. 1986. Dioxin danger from garbage incineration. *Analytical Chemistry* 58: 633A-641A.
- Kuehl, D.W., P.M. Cook, A.R. Batterman, D. Lothenbach and B.C. Butterworth. 1987. Bioavailability of polychlorinated dibenzo-p-dioxins and dibenzofurans from contaminated Wisconsin River sediment to carp. *Chemosphere* 16: 667-679.
- Marklund, S., C. Rappe, M. Tysklind and K.-E. Egeback. 1987. Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoline. *Chemosphere* 16: 29-36.
- Munns, W.R., Jr., J.F. Paul, V.J. Bierman, Jr., W.R. Davis, W.B. Galloway, G.L. Hoffman, R.R. Payne, P.F. Rogerson and R.J. Pruell. In preparation. Exposure Assessment Component of the Field Verification Program: Data Presentation and Synthesis. US Environmental Protection Agency, Narragansett, RI.
- O'Keefe, P., D. Hilker, C. Meyer, K. Aldous, L. Shane, R. Donnelly, R. Smith, R. Sloan, L. Skinner and E. Horn. 1984. Tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofurans in Atlantic Coast striped bass and in selected Hudson River fish, waterfowl and sediments. *Chemosphere* 13: 849-860.

- Petty, J.D., L.M. Smith, P.-A. Bergqvist, J.L. Johnson, D.L. Stalling and C. Rappe. 1983. Composition of Polychlorinated Dibenzofuran and Dibenzo-p-dioxin Residues in Sediments of the Hudson and Housatonic Rivers. In G. Choudhary, L.H. Keith and C. Rappe (Eds.). Chlorinated Dioxins and Dibenzofurans in the Total Environment. Butterworth Publishers: Woburn, MA. pp. 203-207.
- Rogerson, P.F, S.C. Schimmel and G. Hoffman. 1985. Chemical and Biological Characterization of Black Rock Harbor Dredged Material, Technical Report D-85-9, prepared by US Environmental Protection Agency, Narragansett, RI, for the US Army Engineer Waterways Experiment Station, Vicksburg, MS. 110 pp.
- Safe, S., G. Mason, B. Keys, K. Farrell, B. Zmudzka, T. Sayer, J. Piskorska-Pliszczyńska, L. Safe, M. Romkes and S. Bandiera. 1986. Polychlorinated dibenzo-p-dioxins and dibenzofurans: Correlation between in vitro and in vivo structure-activity relationships (SARs). Chemosphere 15: 1725-1731.
- Tschirley, F.H. 1986. Dioxin. Scientific American, 254:29-35.
- Umbreit, T.H., E.J. Hesse and M.A. Gallo. 1986. Bioavailability of dioxin in soil from a 2,4,5-T manufacturing site. Science 232: 497-499.

Table 1. The Stable Carbon Isotope Labeled Compounds Spiked into Each Sample.

<u>Compound</u>	<u>Amount (ng)</u>
2,3,7,8-tetrachlorodibenzo-p-dioxin- $^{13}\text{C}_{12}$	19.1
1,2,3,7,8-pentachlorodibenzo-p-dioxin- $^{13}\text{C}_{12}$	23.5
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin- $^{13}\text{C}_{12}$	12.5
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin- $^{13}\text{C}_{12}$	44.4
octachlorodibenzo-p-dioxin- $^{13}\text{C}_{12}$	25.5
2,3,7,8-tetrachlorodibenzofuran- $^{13}\text{C}_{12}$	21.2
1,2,3,7,8-pentachlorodibenzofuran- $^{13}\text{C}_{12}$	12.4
1,2,3,4,7,8-hexachlorodibenzofuran- $^{13}\text{C}_{12}$	15.0
1,2,3,4,6,7,8-heptachlorodibenzofuran- $^{13}\text{C}_{12}$	37.5

Table 2. HRGC/HRMS Operating Parameters

Mass Resolution	9,000-12,000 (M/ M, 10% valley definition)
Electron Energy	70 eV
Accelerating Voltage	6,000 Volts
Source Temperature	200 C
Preamplifier Gain	10^{-7} amps/volt
Electron Multiplier Gain	-10^6
Transfer Line Temperature	280°C
Column	DB-5 60M
Injector Temperature	300°C
Column Temp - Initial	160°C Hold for 2 min
Column Temp - Program	20°C/min to 240°C hold for 30 min 20°C/min to 320°C hold for 20 min
Carrier Gas	Helium
Flow Velocity	~30 cm/sec
Injection Mode	Splitless
Injection Volume	2 l

Table 3. Exact Masses Used for the Determination of PCDD and PCDF

Compound	Accurate Mass		Theoretical Isotope Ratio Mass 1/Mass 2
	Mass 1	Mass 2	
Tetrachlorodibenzo-p-dioxins	319.8965	321.8936	0.77
Tetrachlorodibenzofurans	303.9016	305.8987	0.77
Pentachlorodibenzo-p-dioxins	355.8546	357.8517	1.54
Pentachlorodibenzofurans	339.8597	341.8567	1.54
Hexachlorodibenzo-p-dioxins	389.8156	391.8127	1.23
Hexachlorodibenzofurans	373.8207	375.8178	1.23
Heptachlorodibenzo-p-dioxins	423.7766	425.7737	1.03
Heptachlorodibenzofurans	407.7817	409.7788	1.03
Octachlorodibenzo-p-dioxins	457.7377	459.7347	0.88
Octachlorodibenzofurans	441.7428	443.7398	0.88
Tetrachlorodibenzo-p-dioxin- ¹³ C ₁₂	331.9367	333.9338	0.77
Tetrachlorodibenzofuran- ¹³ C ₁₂	315.9418	317.9389	0.77
Pentachlorodibenzo-p-dioxin- ¹³ C ₁₂	367.8948	369.8918	1.54
Pentachlorodibenzofuran- ¹³ C ₁₂	351.8999	353.8969	1.54
Hexachlorodibenzo-p-dioxin- ¹³ C ₁₂	401.8558	403.8529	1.23
Hexachlorodibenzofuran- ¹³ C ₁₂	385.8609	387.8580	1.23
Heptachlorodibenzo-p-dioxin- ¹³ C ₁₂	435.8168	437.8139	1.03
Heptachlorodibenzofuran- ¹³ C ₁₂	419.8219	421.8190	1.03
Octachlorodibenzo-p-dioxin- ¹³ C ₁₂	469.7779	471.7749	0.88

Table 4. Levels of PCDD/PCDF in Sediment Samples

Sample	Units	2378 Tetra -CDD	Total Tetra -CDD	12378 Penta -CDD	Total Penta -CDD	123678 Hexa -CDD	Total Hexa -CDD	123678 Hepta -CDD	Total Hepta -CDD	Octa -CDD
BH-Original Compos. BB	ng/g	<0.078	0.15	0.073	0.39	0.088	0.95	1.29	2.98	13.0
BH-Wetland Site July 85	ng/g	0.043	0.19	0.072	0.34	0.073	0.83	1.16	2.56	11.4
BH-Upland Site	ng/g	<0.11	0.15	0.076	0.16	0.065	0.99	1.13	2.54	10.4
RS8510 ^a	ng/g	<0.014	0.0027	<0.012	0.004	0.008	0.11	0.16	0.38	1.2
2E8510 ^b	ng/g	<0.02	0.032	0.018	0.087	0.021	0.25	0.36	0.79	3.2
Laboratory Native Spike ^c	ng/sample	8.85	8.85	9.29	9.29	7.12	8.53	21.6	21.6	21.8
Laboratory Method Blank ^d	ng/g	<0.012	<0.012	<0.004	<0.004	<0.003	<0.003	0.004	0.004	0.01

^a RS8510 - Reference site collected 10/85.

^b 2E8510 - 200 meters east of the mound center collected 10/85.

^c Spiked with 9.5 ng each of 2,3,7,8-tetra-CDD, 1,2,3,7,8-penta-CDD, 1,2,3,6,7,8-hexa-CDD and 23.75 ng each of 1,2,3,4,6,7,8-hepta-CDD and 1,2,3,4,6,7,8,9-octa-CDD.

^d An 11 gram sample size was assumed.

Table 4. (Continued)

Sample	Units	2378 Tetra -CDF	Total Tetra -CDF	12378 Penta -CDF	Total Penta -CDF	123478 Hexa -CDF	Total Hexa -CDF	1234678 Hepta -CDF	Total Hepta -CDF	Octa -CDF
BH-Original Compos. BB	ng/g	0.25 ^a	2.3	0.039	1.46	0.15 ^a	0.77	0.54	0.98	1.38
BH-Wetland Site July 85	ng/g	0.25 ^a	2.0	0.046	1.38	0.18 ^a	0.86	0.65	1.29	2.42
BH-Upland Site	ng/g	0.24 ^a	3.1	0.041	2.5	0.19 ^a	1.3	0.73	1.34	1.94
RS8510	ng/g	0.024 ^a	0.14	0.005	0.06	0.006 ^a	0.04	0.05	0.11	1.65
2E8510	ng/g	0.07 ^a	0.56	0.015 ^a	0.34	0.047 ^a	0.25	0.18	0.34	0.74
Laboratory Native Spike ^b	ng/sample	9.02	9.02	9.5	9.5	9.6	9.6	22.6	22.6	26.5
Laboratory Method Blank ^c	ng/g	<0.006	<0.006	<0.002	<0.002	<0.002	<0.002	0.003	0.006	0.03

^a Incomplete resolution of the specific isomer from four coeluting isomers.

^b Spiked with 9.5 ng each of 2,3,7,8-tetra-CDF, 1,2,3,7,8-penta-CDF, 1,2,3,4,7,8-hexa-CDF and 23.75 ng each of 1,2,3,4,6,7,8-hepta-CDF and 1,2,3,4,6,7,8,9-octa-CDF.

^c An 11 gram sample size was assumed.



Table 5. Number of Peaks Quantified as PCDD/PCDF in Each Congener Class

Sample	TOTAL TETRA -CDD		TOTAL PENTA -CDD		TOTAL HEXA -CDD		TOTAL HEPTA -CDD		TOTAL TETRA -CDF		TOTAL PENTA -CDF		TOTAL HEXA -CDF		TOTAL HEPTA -CDF	
BH-Original Compos. BB	3		5		6		2		14		11		7		4	
BH-Wetland Site July 85	4		4		6		2		14		13		8		4	
BH-Upland Site	3		1		6		2		13		16		10		2	
RS8510	1		1		5		2		12		9		5		2	
2E8510	2		4		6		2		14		10		6		2	

Table 6. Percent Recoveries of Internal Standards

Sample Number	TETRA-CDD $^{13}\text{C}_{12}$	PENTA-CDD $^{13}\text{C}_{12}$	HEXA-CDD $^{13}\text{C}_{12}$	HEPTA-CDD $^{13}\text{C}_{12}$	OCTA-CDD $^{13}\text{C}_{12}$
BH-Original Compos. BB	64	69	55	50	28
BH-Wetland Site July	84	84	66	54	26
BH-Upland Site	47	39	31	29	17
RS8510	88	92	79	72	28
2E8510	83	73	53	41	18
Native Spike	72	90	81	82	41
Method Blank	72	98	87	86	48

Table 6. (Continued)

Sample Number	TETRA-CDF $^{13}\text{C}_{12}$	PENTA-CDF $^{13}\text{C}_{12}$	HEXA-CDF $^{13}\text{C}_{12}$	HEPTA-CDF $^{13}\text{C}_{12}$
BH-Original Compos. BB	60	72	54	49
BH-Wetland Site July 85	84	79	55	47
BH-Upland Site	41	42	39	26
RS8510	92	98	74	58
2E8510	70	72	46	37
Native Spike	71	77	63	70
Method Blank	68	83	68	74

Table 7. Chlorine Isotope Ratios for Samples
(Theoretical Chlorine Isotope Ratio)

Sample	2378 Tetra -CDD (0.77)	Total Tetra -CDD (0.77)	12378 Penta -CDD (1.54)	Total Penta -CDD (1.54)	123678 Hexa -CDD (1.23)	Total Hexa -CDD (1.23)	123678 Hepta -CDD (1.03)	Total Hepta -CDD (1.03)	Octa -CDD (0.88)
BH-Original Compos. BB	---	0.75	1.44	1.48	1.05	1.25	0.99	1.01	0.92
BH-Wetland Site July 85	0.81	0.79	1.62	1.66	1.38	1.18	1.08	1.06	0.90
BH-Upland Site	---	0.77	1.34	1.41	1.41	1.13	1.09	1.09	0.89
R88510	---	0.72	---	1.47	1.13	1.18	1.12	1.08	0.92
2E8510	---	0.83	1.47	1.53	1.12	1.25	0.99	0.99	0.86
Native Spike	0.82	0.82	1.52	1.52	1.24	1.24	1.05	1.05	0.90
Method Blank	---	---	---	---	---	---	1.13	1.13	0.98

--- Congener class not detected in sample.

Table 7. (Continued)

Sample	2378 Tetra -CDF (0.77)	Total Tetra -CDF (0.77)	12378 Penta -CDF (1.54)	Total Penta -CDF (1.54)	123478 Hexa -CDF (1.23)	Total Hexa -CDF (1.23)	1234678 Hepta -CDF (1.03)	Total Hepta -CDF (1.03)	Octa -CDF (0.88)
BH-Original Compos. BB	0.87	0.79	1.52	1.61	1.27	1.27	1.08	1.01	0.92
BH-Wetland Site July	0.75	0.75	1.65	1.51	1.11	1.20	0.99	1.07	0.96
BH-Upland Site	0.78	0.77	1.45	1.54	1.26	1.23	1.06	1.06	0.87
RS8510	0.75	0.76	1.44	1.50	1.40	1.28	1.16	1.11	0.86
2E8510	0.87	0.77	1.32	1.51	1.21	1.25	0.94	1.03	0.92
Native Spike	0.77	0.77	1.55	1.55	1.23	1.23	1.04	1.04	0.89
Method Blank	---	---	---	---	---	---	0.97	0.93	0.83

---- Congener class not detected in sample.

Table 8.

Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in composited sediment from Black Rock Harbor. The first column contains data from the present study. The second two columns contain results of duplicate analyses conducted at the U.S. Environmental Protection Agency's Environmental Research Laboratory at Duluth, MN (ERL-D)^a. Concentrations as ng/g dry weight.

	<u>This Study</u>	<u>ERL-D</u>	
<u>Dibenzo-p-dioxins</u>			
2,3,7,8-tetra-CDD	<0.078	0.057	0.057
1,2,3,7,8-penta-CDD	0.073	0.094	0.081
1,2,3,6,7,8-hexa-CDD	0.088	0.128	n.d.
1,2,3,4,6,7,8-hepta-CDD	1.29	1.78	1.74
Octa-CDD	13.0	16.1	18.0
<u>Dibenzofurans</u>			
2,3,7,8-tetra-CDF	0.25 ^b	0.057	0.060
1,2,3,7,8-penta-CDF	0.039	0.091	0.070
1,2,3,4,7,8-hexa-CDF	0.15 ^b	0.134	0.134
1,2,3,4,6,7,8-hepta-CDF	0.54	1.07	1.05
Octa-CDF	1.38	2.79	3.09

^a - Data from Norwood et al., In preparation.

^b - Incomplete resolution of the specific isomer from coeluting isomers.

n.d. - not detected.

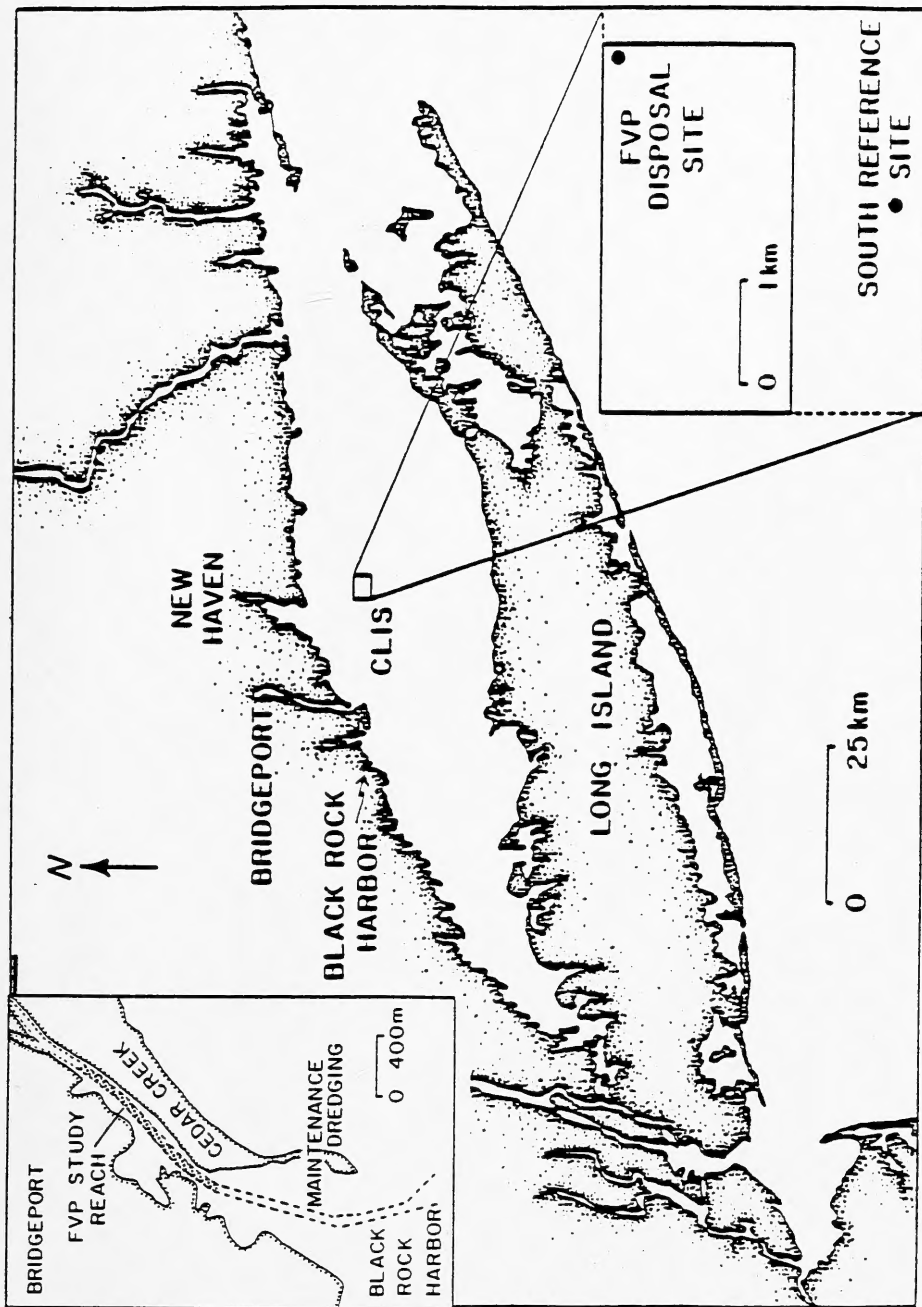


Figure 1. Map of the Field Verification Program study area showing the Study Reach in Black Rock Harbor and the disposal site at the Central Long Island Sound Disposal Area.

